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Alternative spontaneous combustion testing methods

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ALTERNATIVE SPONTANEOUS COMBUSTION TESTING METHODS

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ABSTRACT: The spontaneous combustion of coal is a persistent ongoing risk within the coal mining industry. To assess this risk, coal samples are regularly screened for their propensity to spontaneously combust. Within Australia, the predominant method adopted by the Australian mining industry for assessment is the Adiabatic Self-Heating (R_{70}) test. However, limitations related to the difficulty of inducing the initial stage of self-healing process for low reactive coals, significant testing times, and lack of standardisation of instrumentation have remained present to this day.

Alternative testing methodologies have emerged in the last few years, including: an alternative adiabatic self-heating test using humidified oxygen showing promise for low-reactive coals and the use of simultaneous thermal analysis (STA) to provide thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) within one test.

The modification of the adiabatic self-heating test with sample moisture and gas humidification allows insight into the reaction kinetics under different self-heating environments. A novel adiabatic test with moist sample and humidified oxygen was compared against alternating testing conditions of sample drying/moisture and gas humidification. All testing except one showed a heightened rate of reaction when extrinsic humidity was introduced.

Additionally, combined thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) is able to provide rapid testing results and their proposed spontaneous combustion indicators are shown to provide agreed metrics for a sample's propensity to spontaneously combust when compared with adiabatic self-heating testing. The Burnout Index and Self-Heating Temperature derived from the first-order differential thermogravimetric (DTG) analysis aligned closely with the tested R_{70} values, with a R_2 of 0.851 and 0.953, respectively.

INTRODUCTION

Spontaneous combustion of coal within coal mines still plagues the industry into the 21st century. Even in risk adverse mining conditions found in Australia, the issue still presents a hazard to day-to-day operations and to those that work in mines. Since the early 20th century, quantification of coal's likelihood to spontaneously combust has been sought to mitigate risk (Davis and Byrne, 1924).

In Australia, one of the leading methodologies for assessing the spontaneous combustion propensity of coal is the R_{70} method. The R_{70} methodology was an improvement on prior adiabatic tests, with both the instrumentation and ranking criteria refined to provide a quantitative assessment for spontaneous combustion as a relationship between oxygen exposure, temperature increase and time (Humphreys et al., 1981).

However, there are a few disadvantages of the R_{70} test. The first is the replication of the mining environment, as the R_{70} is conducted with dry samples and dry oxygen rather than coal samples as received or humid oxidizing environment at mine sites. The second is the difficulty of inducing initial stage of self-heating process for low reactive coals. The third is the time to test, with high-ranking coals commonly found within Queensland taking days or weeks to reach the designated 70 °C, if at all, before testing can be conducted. The fourth is the standardisation of the test and of the instrumentation as only a few R_{70} instruments exist, and all have various design differences.

The R_{70} testing methodology relies on the fact that a large dust deposit, in practice, can behave approximately adiabatically (Hattwing and Steen, 2004). The R_{70} attempts to compensate for heat transfer by applying a proportionate amount of thermal energy back to the system and minimising the thermal gradient by matching the internal system's temperature.

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However, by nature of the test, it requires an open system as gas flow into and out of the system is required to sustain the oxidizing atmosphere required, thus allowing the transfer of mass. Additionally, as the instrument is relying on a thermal matching to approximate an adiabatic system, any temperature differential will introduce an error.

Improvements towards R_{70} testing have allowed alternative investigations into how coal behaves with respect to intrinsic and extrinsic factors. The works of Beamish and Beamish (2011) and Wang (2020) have improved the methodology of this test to better replicate the environments that coal is mined in. Beamish and Beamish (2011) proposed the wet adiabatic test methodology that uses the coal within an 'as received state', rather than drying the coal before oxygen exposure. This investigation into a sample's intrinsic moisture aims to assess the influence of inherent moisture within coal with respect to oxygen on the rate of self-heating of a sample.

Wang (2020) looked at testing extrinsic factors, whereas the coal is dried but humidification of the oxygen into the sample is allowed to replicate the humidity present within underground coal mines. Additionally, both tests lowered the amount of oxygen received by the system to 10 mL/min, down from the original 50 mL/min, while increasing the sample mass to 200 g. These changes have shown drastic changes with the self-heating profile of coal samples with slight modifications and have allowed mine operators to better understand the dynamic heating profiles that coal exhibits.

Despite these improvements, the testing regime, which would allow coal operators to gain a better understanding of the propensity of the coal to spontaneously combust within a rapid and accurate manner, is still a limiting factor. To overcome this limitation of testing time, recent research has begun reinvestigating thermogravimetric analysis.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) have been used within the material science industry for decades for understanding the thermal characteristics of materials over a temperature range (Chan et al., 2020). The principle of TGA relies on the sample mass measured over time with respect to an increasing temperature change, while DSC measures the thermal energy required to heat a sample with respect to a known standard. Avila et al. (2014) noted that earlier studies with TGA were influenced by low sample sizes, incorrect heating rates and the noise of early TGA instrumentation. However, Avila et al. (2014) also commented on the technological advancement of the instruments since those studies, which allow higher precision and better low temperature control.

A few benefits of TGA/DSC analysis have potential for their application within the mining industry. Firstly, testing is rapid and does not consume a lot of material: sample sizes are approximately 20 mg and testing can be completed within an hour. Secondly, the instrument is more common and standardised, meaning that testing can be completed at more laboratories with more confidence as a test done at one laboratory is akin to another. Finally, TGA has also been shown to allow the indirect proximate analysis of coal (Beamish, 1994; Wang, 2020).

Several indicators have been proposed to provide an indication of the coal's likelihood for spontaneous combustion during TGA/DSC analysis, as shown in **Table 1**.

Wang (2020) proposes the mass gain from the early heating stage during TG analysis. By taking the difference between the first infliction and second infliction point of the thermogram (Eq. 1), indication of a sample's propensity to undergo oxidation is measured, and the higher the mass gain the lower the propensity.

Table 1: TGA/DSC Spontaneous Combustion Indicators

Spontaneous Combustion Indicator	Thermal Analysis	Definition	Eq.
Mass Gain	TGA	$M_{gain} = M_{T2} - M_{T1}$	(1)
Onset Temperature	DSC	$T_{onset} = T_{DSC=0}$	(2)
Self-heating Temperature	DTA	$T_{sh} = (dw/dt)_{min}$	(3)
Burnout Index	DTA	$D_f = \dfrac{(dw/dt)_{max}}{\Delta t_{1/2} t_p t_f}$	(4)

Pandey et al. (2015) used the DSC to provide an index for coal spontaneous combustion, where the point of the analysis is when the mW per sample mass is equal to zero (Eq. 2). Mohalik et al. (2021) used the first order differential thermographic (DTG) analysis to provide an indication of self-heating of coal at the first inflation point (Eq. 3). Ma et al. (2006) use a method called the Burnout Index (Eq. 4) to investigate the rate of ignition.

However, the research into comparisons of the TGA results against established metrics is still within its infancy. While established rankings exist for R_{70} testing, only proposed rankings exist for TGA. By evaluating samples with established rankings to new testing methods, a comparison can be drawn to allow the use of these new indexes as alternative spontaneous combustion assessments. As the R_{70} method is the more established testing methodology within Australia, it was chosen as the comparison method.

This paper presents the application of the additional testing methodologies to the adiabatic tests currently undertaken and the assessment of the basic reaction kinetics introduced by sample moisture and humidification of the gas.

Additionally, an evaluation into TGA/DSC spontaneous combustion indicators as a rapid and more accessible analysis for the assessment of spontaneous combustion propensity for coal samples was investigated.

A correlation study between the TGA/DSC indicators and tested R_{70} values was conducted, showing Burnout Index and Self-Heating Temperature had a strong correlation, with a R_2 of 0.851 and 0.953, respectively.

METHODOLOGY

Sample Preparation

Four coal samples from the Bowen Basin region were used for the analysis by thermogravimetry along with adiabatic analysis. Samples were screened to ensure that they had particularly low or medium-low reactivities when screened with the original adiabatic testing methodology. Additionally, the samples were known to be fresh to avoid the issues of premature storage oxidation.

The samples were crushed to <4 mm using Jaques laboratory jaw crusher (model 127ST), and then milled to <250 µm using a Retsch Cross Beater mill (model WRB 80 c/2q SIL).

Proximate Analysis

A sub-allocate of the <4mm sample was provided to an external laboratory for proximate analysis. ISO 11722, ISO 1171 and ISO 562 were referred during analysis.

Adiabatic Testing

Within a laboratory dehydrating oven, a 1000 mL conical flask was equipped with a rubber stopper that was modified with a gas inlet and gas outlet and placed inside with 150 g of <250 µm milled coal. Nitrogen (N_2) with a flowrate of 250 mL/min was passed over the sample for one hour at room temperature (25 °C +/- 5 °C), and then for 16 hours at 110 °C. The sample was allowed to return to 40 °C +/- 2 °C, then transferred to a 473 mL (16 oz) Dywer flask equipped with a PTFE stopper and placed into an adiabatic oven that was resting at 40 °C. N_2 with a flowrate of 50 mL/min was passed over the coal sample until the sample had equilibrated with the oven at 40 °C (+/- 0.8 °C). The oven was then switched to adiabatic mode, where 50 mL/min of Oxygen (O_2) was passed into the sample, and the set point of the oven was determined by the sample temperature. The testing continued until the sample passed 70 °C, 72 hours had passed, or the sample failed to show any signs of self-heating, whichever came first.

For the modified adiabatic tests, modifications to the above procedure were made by the reduction of the oxygen flow rate during adiabatic mode to 10 mL/min. The sample was not dried prior to testing during the moist adiabatic and combined adiabatic tests. Additionally, the O_2 was humidified by an Ankersmid humidifier AHU prior to introduction to the sample during the humid and combined adiabatic tests.

TGA Analysis

For the experimental analysis of the coal samples from the Bowen Basin, a Netzsch STA 449 F3 Jupiter was used for the TGA analysis. The testing was provided by an external party as the instrumentation was not available internally. The external party conducted testing to requested conditions. The instrumentation provided both TGA and DSC.

For each sample, approximately 20 mg of coal milled to <250 μm was tested. The parameters for the testing conducted specified a heating rate of 10 K/min from 40 °C to 800 °C, with a mixture of 1:4 oxygen and nitrogen with a flowrate of 20 mL/min fed into the reaction chamber and with 20 mL/min of argon as a blanket.

RESULTS

Four samples from the Bowen Basin region underwent proximate analysis, as shown in **Table 2**. The proximate analysis provided a base overview of the coal content.

Table 2: Proximate Analysis

Sample	Fixed Carbon (ad%)	Volatile Matter (ad%)	Moisture (ad%)	Ash (ad%)
BB1	56.5	31.9	2.8	8.8
BB2	65.9	21.3	1.9	10.9
BB3	46.5	23.6	2.2	27.7
BB4	61.4	17	1	20.6

The samples tested were subjected to the normal, moist, humid, and combined adiabatic test conditions, along with TGA analysis. As shown in **Table 3**, the adiabatic testing results were provided in °C/h, while the TGA indicators were provided by mass gain (M_{Gain}), Self-Heating Temperature (T_{sh}), Onset Temperature (T_{onset}) and Burnout Index (D_f), using the Equations listed in **Table 1**.

Table 3: Spontaneous Combustion Indicator Results

Sample	Adiabatic Indicators				Thermal Analysis Indicators			
	Normal (°C/h)	Moist (°C/h)	Humid (°C/h)	Combined (°C/h)	M_{Gain} (%)	T_{sh} (°C)	T_{onset} (°C)	D_f (°C)
BB 1	1.42	0.1	1.5	0.82	2.31	250.07	172.23	434.74
BB 2	0.34	-	0.27	0.1	2.12	299.99	191.78	472.72
BB 3	0.71	0.01	1.29	0.46	1.85	275.02	173.89	448.19
BB 4	0.28	-	0.31	0.26	2.76	309.97	208.49	486.99

DISCUSSION

Adiabatic Testing

For the adiabatic testing, a simplified relationship was used (Eq. 5) to explain the effect the variables had on the overall enthalpy of the system as:

$$H_{R70} = \sum_k H_k + c \qquad \textbf{(5)}$$

where: H_{R70} is the total enthalpy of all the subsystems, k refers to the constituents of a system, H_k refers to the enthalpy of the reaction vessel system and c is a designation of the instrumentation (exterior) system.

The overall enthalpy of each subsystem (Eq. 6) can be summarised as:

$$\sum_k H_k = H_{Oxidation} + H_{Rewetting} + H_{Evaporation} \quad \textbf{(6)}$$

where: the total enthalpy sum of the reaction vessel system is from oxidation, rewetting, and evaporation. The standard adiabatic test has only one constituent towards the enthalpy of the system, oxidation ($H_{Oxidation}$). However, when the sample was not dried to remove its intrinsic moisture and the oxygen entered the system with extrinsic humidity, these additional constituents, ($H_{Rewetting}$ and $H_{Evaporation}$), had additive or subtractive effects on the overall system enthalpy. Wang et al. (2018) describes the overall thermodynamics of the reaction with greater detail.

Figure 1 highlights the different rate of reactions that occur when these subsystems are added or subtracted from coal samples BB 1 to BB 4. As shown in **Figure 1**, the introduction of humidity to the oxygen allowed the heat of rewetting phenomenon to drive the rate of reaction faster in all systems except for the 'BB 2' dried coal and humidified oxygen test. Subsequently, the additional heat of rewetting and the inherit oxidation enthalpy were able to overcome the enthalpy of evaporation in all samples tested.

The introduction of sample moisture compared to the typical removal of sample moisture had a detrimental effect on the overall rate of reaction. In all tests, samples left in their 'as received' state had lower rates of reaction compared to the dried samples. However, the combination of inherit sample moisture and humidification of the oxygen increased the rate of reaction significantly. It is suggested that the phenomenon of the enthalpy of rewetting was able to provide the required activation energy to initiate and accelerate the coals' oxidation process.

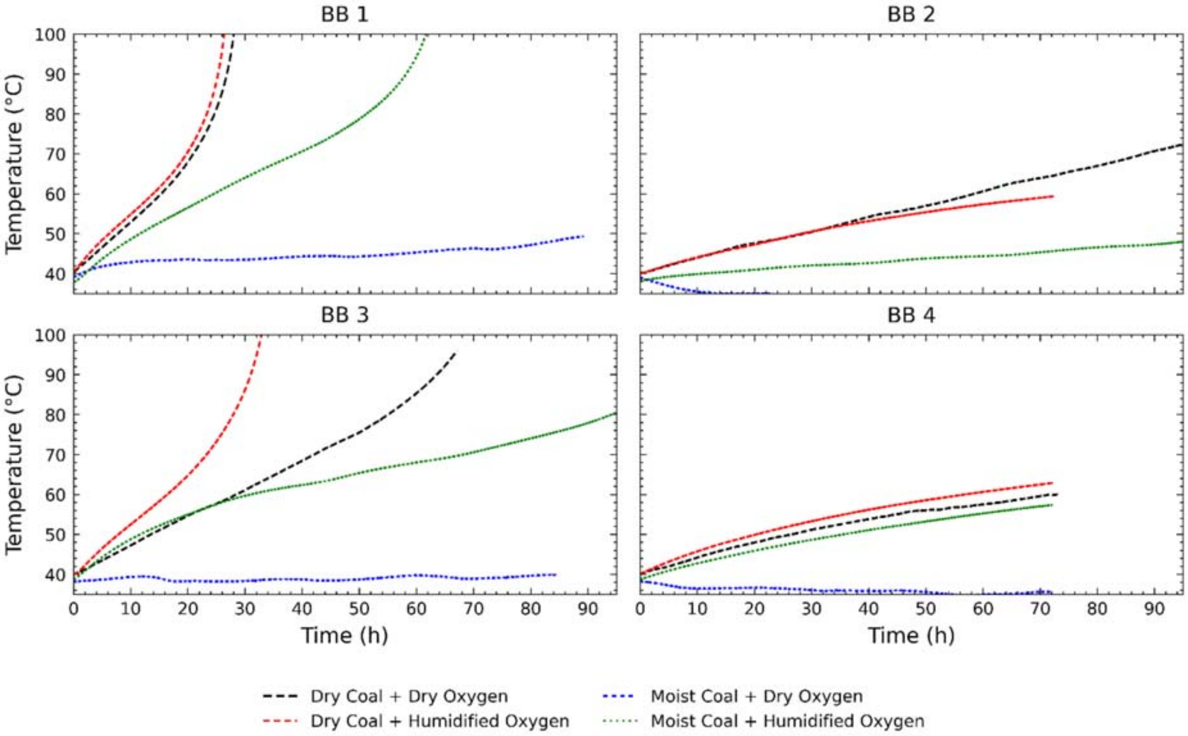

Figure 1: Adiabatic Testing of Bowen Basin Coal Samples

For sample 'BB 2', while the heat of rewetting did not increase the reaction rate for the dried sample, it did increase it for the sample with inherit moisture. This phenomenon is likely due to the decreased evaporation that can occur within a system when humidity is present. When samples 'BB 1' to 'BB 4' were tested in their 'as received' state of moisture, all samples experienced a drastic increase of heating rate compared to the moist coal samples in the presence of dried oxygen. This effect could be attributed to the reduced evaporation rate as the humidity of the environment was increased, thus reducing the effect of enthalpy of evaporation on the system.

A flaw within this testing methodology is that gas humidification was assumed and not measured during the test. While complete saturation is unlikely, Wang et al. (2018) provided background that assures a high degree of humidity presence within the inlet oxygen stream. However, further testing should be undertaken to measure this degree of humidification.

Overall, the alternation of sample drying and oxygen humidification highlights the importance of replicating environmental conditions in laboratory testing. Spontaneous combustion tests may underestimate the risk of spontaneous combustion if intrinsic and extrinsic factors influencing the coal spontaneous combustion are ignored.

Thermogravimetric Analysis

Figure 2 shows the overall profile of the TG, DTG and DSC analyses undertaken on the four Bowen Basin samples. The TG and DSC analyses were left unprocessed, while a Savitzky-Golay Filter with a 2^nd^ order polynomial and a moving 5 data points was used for the DTA as slight noise was introducted in the data by taking the derivative.

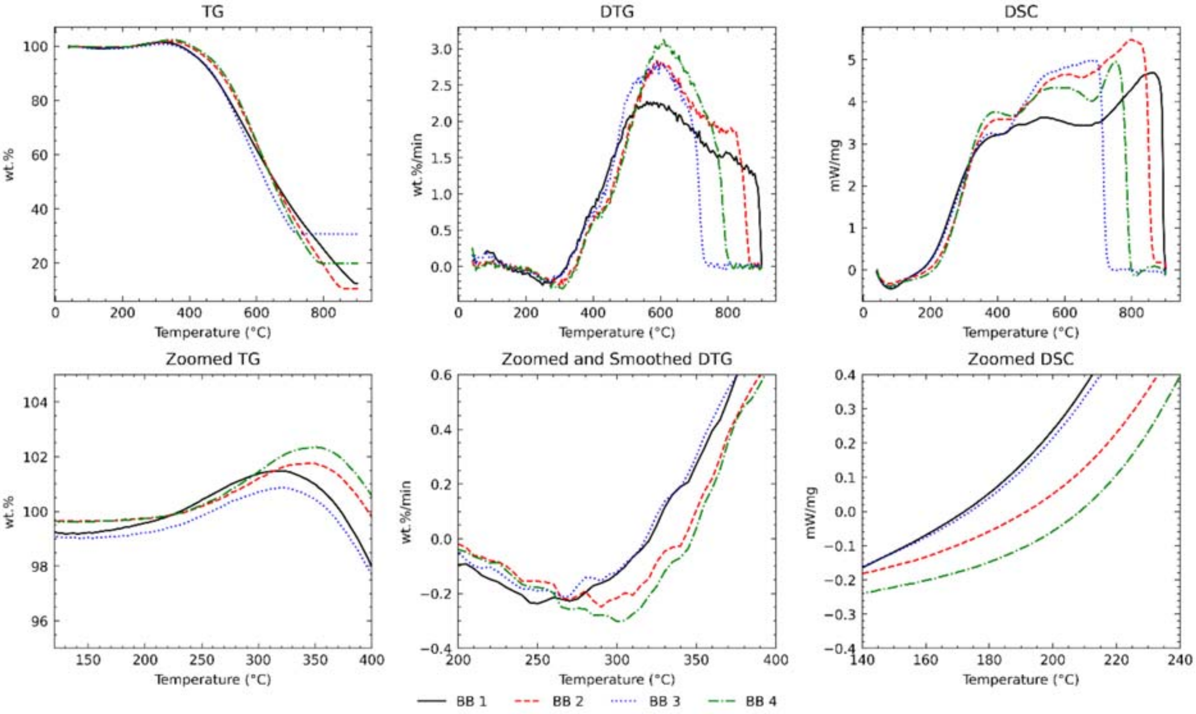

Figure 2: TG/DTG/DSC Profiles of Bowen Basin Coal Samples

Using the indicators provided within **Table 1**, rankings can be provided that can be compared to that of a known scale, such as the R_{70} analysis. By plotting the corresponding indicators against the R_{70} values (**Figure 3**), a preliminary comparison was undertaken to assess the reliability of the TG, DTG and DSC derived indicators.

For the Burnout Index (D_f) and the Self-heating Temperature (T_{sh}) parameters, the values align closely with the tested R_{70} values, with a R_2 of 0.851 and 0.953, respectively. The T_{Onset} has a less strong correlation with R_2 of 0.644, while the M_{Gain} did not show any correlation within the samples tested.

From the preliminary analysis, both TGA and DSC would serve as potential spontaneous combustion assessment methods if a large cross comparative study were to be undertaken of samples of known reactivity. It should, however, be noted that the limitation of the small sample size on the strength of such analysis could skew the regression. As such, further analysis would require a larger sample size to verify the relationship.

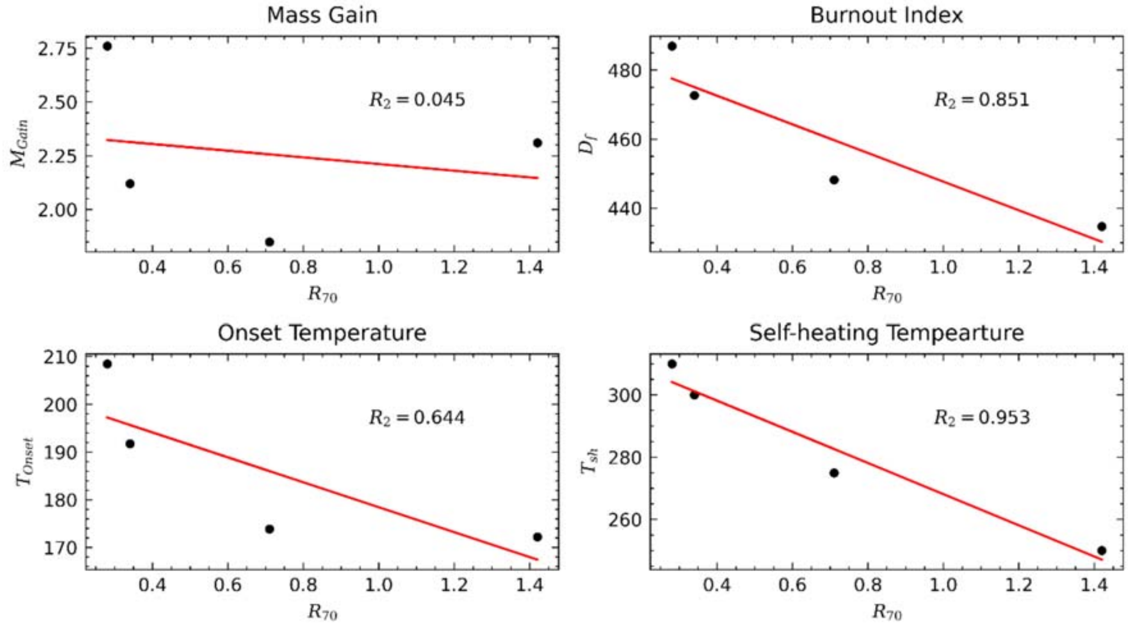

Figure 3: Linear Regression of TGA/DSC Indicators

CONCLUSIONS AND RECOMMENDATIONS

Within this paper, four Bowen Basin samples were tested with the original adiabatic methodology provided by Humphreys et al. (1981), the modified procedures evaluated by Beamish and Beamish (2010) and Wang (2020), and the combined adiabatic methodology. The testing highlighted the additive and subtractive effects that the intrinsic moisture and extrinsic humidity might have on the spontaneous combustion of coal. The humidification of the oxygen increased the rate of reaction for all tests except for sample BB 2 that had been dried prior to testing. Additionally, the intrinsic sample moisture decreased the rate of reaction for all samples compared to the dried samples while the introduction of humidity to the test reduced the effects of the enthalpy of evaporation.

By testing the influence of humidity introduced into testing, the kinetics of rewetting and evaporation specific to coal seams can be investigated. This can provide more understanding on how changing atmospheric conditions can influence self-heating events within an underground environment. The use of humidified oxygen with dried coal could be used as an accelerated R_{70} test to help expedite the lengthy testing times according to the original methodology. Additionally, by comparing sample heating events with humidified gas, weather and atmospheric changes can be considered.

The preliminary investigation into TGA as a quicker and more cost-effective spontaneous combustion test showed promising results, with agreement between the results derived from TGA and the R_{70} rankings. The Burnout Index and Self-Heating Temperature indicators provided a strong correlation with the R_{70} values within this small-scale study.

A major limitation of the thermogravimetric testing was that testing had to be conducted off-site, and, thus, premature sample oxidation might have been introduced. Attempts to reduce the influence of premature oxidation were made by removing all headspace within the sample container and keeping the temperature near 0 °C during transport and storage. However, it is likely that the reactivity of the samples was reduced and, thus, this limitation can be removed by having access to instrumentation on-site.

Future testing should be conducted with a wide spectrum of samples from Australian and international mining regions to allow accurate qualitative ranking for spontaneous combustion propensity. Ideally, an instrument should be available within the same laboratory to reduce the premature oxidation of samples along with ensuring that quality control is maintained throughout the process. Additionally, all indicators should be screened as better trending can be undertaken with a more diverse dataset.

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